

RESEARCH PAPER RP973

*Part of Journal of Research of the National Bureau of Standards, Volume 18,
February 1937*

SIMPLIFIED DETERMINATION OF RESIN IN PAPERS AND PULPS

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ABSTRACT

A method is given for the simple and precise determination of resin in papers which have been surface-sized with glue or starch, coated with casein-clay emulsion, or not surface-sized or coated. The extracting solution is 95-percent ethyl alcohol acidified with hydrochloric acid in the ratio 4 ml of concentrated HCl: 1,000 ml of alcohol. The extract is dissolved in anhydrous ether, so that the usual laborious and time-consuming washing of the ether solution with water to eliminate the nitrogenous sizing or coating materials is avoided. The method is applicable also to the determination of natural resins in wood pulps. The equivalent weight of the extracted resin, based on the oxidation by dichromate, is made the basis for a new criterion of the purity of the extract.

CONTENTS

	Page
I. Introduction.....	227
II. Acidity of the solvent and the treatment of the alcoholic extract.....	228
III. New method of extraction in detail.....	229
IV. Experimental results and discussion.....	230
1. Equivalent weight of the extract.....	230
2. Pulps and the uncoated and nonsurface-sized papers.....	231
(a) Paper stock with known amounts of rosin.....	231
(b) Comparison with the results of other methods on various pulps and papers.....	232
3. Coated and surface-sized papers.....	233

I. INTRODUCTION

The method in general use at present for the quantitative determination of resin¹ is that of the Technical Association of the Pulp and Paper Industry, known as TAPPI tentative standard T408m, and referred to subsequently as the TAPPI method in this paper. In this method the extracting solvent is acidulated alcohol (95-percent alcohol, 90 percent; glacial acetic acid, 0.5 percent; water, 9.5 percent; by volume). If nitrogenous materials are present in the paper, the alcoholic solution must be evaporated to dryness and the residue extracted with ether. This ether solution of resin must then be washed with two or more portions of water. If no nitrogenous materials are present, the alcoholic solution is simply evaporated to dryness and the residue weighed as resin.

¹ In this article both natural resins occurring in wood pulps and rosin added to the paper will be referred to as "resin", unless the specific instance requires a distinction to be made.

Since the TAPPI method was used in the present work for purposes of comparison only on materials containing no surface-sizing or coating, such as glue, starch, or casein, the ether extraction was omitted. The alcoholic extracts were filtered, however, the omission of which process constitutes an obvious shortcoming of the TAPPI method. Furthermore, the time of extraction was extended to 2 hours at the rate of 15 siphonings an hour, which is much more than the TAPPI method calls for.

Extraction by the TAPPI method has been shown by Sutermeister and Torrey² to be incomplete. They developed a method in which they recommended the use of a solution of the composition 25 ml of concentrated sulfuric acid to 1,000 ml of 95-percent ethyl alcohol, and used a preliminary 5-hour period of steeping, and an 8-hour period of actual extraction.

II. ACIDITY OF THE SOLVENT AND THE TREATMENT OF THE ALCOHOLIC EXTRACT

The function of the acid is to resolve the aluminum-rosin aggregate into its components, thus allowing the rosin to dissolve in the alcohol. According to the work of Sutermeister and Torrey, acetic acid does not furnish sufficient hydrogen ion to accomplish this, which is in accord with the findings of the present work. The use of sulfuric acid requires, however, the long steeping and extraction periods, both of which are somewhat impractical for the routine analysis of large numbers of samples. When sulfuric acid is used, the steeping and long extraction seem to be necessary for the reason that the acid is nonvolatile under the conditions of extraction, and is soon almost completely washed out of the siphon cup. It was found in this laboratory that the sulfuric-acid concentration, initially 0.9*M*, decreases to 0.001*M* in the siphon cup after the first half hour of distillation, when measured with a glass electrode in the presence of the paper.

To obviate these difficulties the strong volatile hydrochloric acid was used in the present work. By the use of this acid the extraction, without preliminary steeping, was found to be practically complete in 2 to 2½ hours. Furthermore, the partial neutralization of the acid before evaporation of the solvent, necessary when sulfuric acid is used, is not necessary when hydrochloric acid is the acidulant, because this acid evaporates along with the alcohol without becoming sufficiently concentrated to attack the resinous material significantly. This was found by separate experiments in which rosin of known weight in alcoholic hydrochloric acid was evaporated to dryness, dissolved in ether, reevaporated, and weighed. The change in weight was negligible when compared with that of the control experiment, in which no acid had been used.

In the present work the simple "Underwriter" equipment was used. When the strongly acidic solution recommended by Sutermeister and Torrey was employed under these conditions, large quantities of the products of the hydrolysis of cellulose were formed which had to be separated from the resin by the usual water-washing of the ether extract in separatory funnels. To avoid this, it was necessary to use a lower acidity, which would have to be higher than that of the TAPPI solvent, however, to allow acceptably complete extraction.

² E. Sutermeister and W. V. Torrey, *Paper Trade J.* **94**, 33 (January 21, 1932).

A concentration of hydrochloric acid in the alcoholic solvent, favorable from the standpoints just discussed, was arrived at in the following manner.

The acidity of the TAPPI solvent in the siphon cup was measured with the glass electrode. The hydrogen-ion concentration (more exactly, the activity, calculated directly from the observed pH) was found to be 0.00003*M*. Accordingly, an acidity range above 0.00003*M* was investigated. It was found by trial that a 0.4-percent (by volume) solution consisting of 4 ml of concentrated (35 to 37 percent) HCl and 1,000 ml of 95-percent ethyl alcohol gave maximum extraction of resin with minimum extraction of other substances. A 1.2-percent alcoholic hydrochloric acid solution yielded no more resins, but gave a much larger amount of the hydrolysis products of cellulose, which made subsequent steps more difficult. An 0.08-percent solution gave incomplete extraction (90 percent) on papers. The pH of the siphon-cup distillate from the 0.4-percent solution was found to be 2.2, corresponding to an acidity of 0.006*M*.

Finally, the alcoholic extract often contains, along with the resin, finely divided foreign matter. This is best coagulated by dehydration through brief heating of the residue in the drying oven. After this treatment, the resin dissolves readily in the anhydrous ether, and the material which goes into suspension settles out on short standing. The ether solution is then easily filtered.

III. NEW METHOD OF EXTRACTION IN DETAIL

Five to seven grams of the paper or pulp is cut into strips approximately 5 by 40 mm and placed lengthwise into the Underwriter siphon cup. The extracting solution is made up in the ratio 4 ml of concentrated 35 to 37 percent reagent grade HCl:1,000 ml of 95-percent ethyl alcohol. The hydrochloric acid may be omitted in the case of wood pulps.

The extraction process is continued for approximately 2 hours at the rate of 15 siphonings an hour (equal to 500 ml in the apparatus used) for uncoated and nonsurface-sized papers and pulps, and for 2½ hours when glue, starch, or casein is present. The alcoholic solution is evaporated to dryness, preferably on a steam bath, until acid odors are no longer noticeable. The residue is then heated in a drying oven at 100° C for 15 minutes. After cooling, 20 ml of anhydrous ether is added. The resinous material dissolves very rapidly (5 to 30 seconds) but care should be taken that none remains covered by foreign materials. After standing 15 to 20 minutes to further the coagulation and settling out of the foreign matter, if necessary, the ether solution is filtered with suction through a fine-pore filter paper cut to fit a Gooch crucible, directly into a weighed beaker. It is usually necessary to refilter the filtered solution through the same paper. Another 20-ml portion of ether is used for rinsing. The ether is conveniently evaporated under reduced pressure with the beaker placed in water at 40° C. Fifteen minutes in the drying oven at 100° C will then suffice to remove moisture. Still more rapid, however, is evaporation in a strong current of air, after which the drying time must be lengthened to 30 minutes, as water is condensed from the air by cold ether. The residue is then weighed to the nearest milligram.

If the paper contains fillers, such as ZnS, CaSO₃, and CaCO₃, that react with acids, the sheet, previously weighed, is dipped into normal

aqueous hydrochloric acid solution and allowed to drain for 5 minutes. It is then placed upon a suitable surface and washed free from acid with tap water. After drying, the paper is cut into strips and extracted in the manner just described.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

1. EQUIVALENT WEIGHT OF THE EXTRACT

It became necessary to test the extracts for the presence of probable foreign substances, such as clay or other inorganic salts, including those soluble in water, the products of the hydrolysis of cellulose, and coating and surface-sizing materials, such as glue, starch, and casein. It was found that a suitable test was the oxidimetric equivalent weight, which is simply the number of grams of the extract which will reduce one equivalent, $49.03 \text{ g} = 1/6 \text{ mole}$, of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. The actual completeness of the reaction, that is, whether or not all carbon is oxidized to carbon dioxide, was not investigated extensively, except that acceptable checks were obtained with known weights of various grades of rosin. The equivalent weight of a sample of papermakers' rosin, grade *F*, in the form of an emulsion prepared in the National Bureau of Standards paper mill by saponification with hot sodium carbonate and subsequent dilution, was determined as follows:

5.00 ml of emulsion was neutralized with 0.4-percent alcoholic hydrochloric acid, an excess of the latter was added, and the mixture evaporated to dryness on the steam bath. After further drying for 15 minutes in an oven at 100°C and cooling, the rosin was extracted with anhydrous ether. This solution was evaporated, the residue dried as before, cooled and weighed. Twenty-five ml of concentrated sulphuric acid was then poured over the rosin and allowed to stand 1 hour with frequent agitation. The rosin dissolved without oxidation, as shown by separate experiments wherein the time of standing was increased tenfold with negligible change in the equivalent weight of the rosin. The solution was slowly poured into a 400-ml beaker containing 30.00 ml of standard $1.835N$ potassium dichromate solution, 25 ml of additional sulphuric acid was added, followed by 20 ml of water, and the solution was kept at 150 to 155°C for 20 minutes, air being constantly bubbled through it to prevent bumping. The solution was then diluted twofold, cooled to 60°C or lower, and the remaining dichromate determined electrometrically with ferrous ammonium sulphate.

The results with this method are shown in table 1.

TABLE 1.—*Equivalent weight of a sample of papermakers' rosin, grade F, after saponification*

Weight of rosin	Volume $1.835N$ dichromate used	Equivalent weight
g	ml	g
0.159	24.1	3.60
.160	24.3	3.57
.160	23.5	3.71
	Average.	3.63

The value 3.63 is in good agreement with the equivalent-weight values of the extracts from all types of papers studied (see table 5). An extract is thus considered "pure" in this work if its equivalent weight is approximately 3.6.³ All of the impurities listed above would raise this value. Clay, if present to the extent of 10 percent in the extract, would raise it to 4.0. Cold or hot water-soluble materials found by the writer to be present to 1.1 to 1.2 percent in the soda and sulfite pulps studied, and found to have equivalent weights of 10.1 and 9.0, would obviously raise the value. The same applies to the hydrolysis products of cellulose, which have an equivalent weight of 6.8,⁴ the same, of course, as cellulose. Finally, starch has the same value as cellulose, whereas the glue and casein used in the papers have equivalent weights of 7.1 and 5.7, respectively, both of which were experimentally determined in this laboratory.

2. PULPS AND THE UNCOATED AND NONSURFACE-SIZED PAPERS

(a) PAPER STOCK WITH KNOWN AMOUNTS OF ROSIN

A purified sulfite pulp, known on the market as "alpha pulp", was beaten for 3 hours in a semicommercial beater in the National Bureau of Standards' paper mill. More water was then added until the weight of the stock constituted 2.5 percent of the whole. The mixture was then stirred for 1 hour, after which 10.00 ml of analyzed⁵ rosin emulsion, prepared in the same paper mill by the usual process, was pipetted in and stirred for 1 hour. Alum solution was then added until the pH became 4.1. After the mixture had been stirred 1 hour more it was filtered on a large Büchner funnel, dried, cut into three equal piles of strips, and analyzed for rosin by the new method. The filtrate, 700 ml., was acidified and the rosin determined by extraction with ether. A like quantity of pulp was dried and analyzed for natural resins.⁶ The results are given in table 2.

TABLE 2.—Analytical data for paper stock with known amounts of rosin

Rosin added (g).....			0.3490
Natural resins (g).....			.0087
Total (g).....			.3577
Rosin in filtrate (g).....			.0245
Resins in fibers (g).....			.3332
Weight of dry cake (g).....			17.40
Therefore, resins in cake (%).....			1.92
Portions taken for analysis (g).....	5.38,	5.82,	6.20
Resins recovered (g).....	.1020,	.1095,	.1170
Therefore, resins found (%).....	1.90,	1.88,	1.89
Average (%).....			1.89

It is seen from the values for the rosin present, 0.3332 g, and the resin found, 0.3285 g, that the recovery is 98.5 percent.

³ A much paler and better grade of rosin was found to give the equivalent-weight values of 3.38, 3.32, 3.34; average 3.35.

⁴ This was determined as follows: Sulfite paper in a siphon cup was steeped overnight in a 3.9-percent alcoholic solution of hydrochloric acid. The usual process for resin extraction was then carried out, but with this solution, after which the alcoholic solution was filtered, evaporated to dryness, weighed, and the equivalent weight determined. The tarry residue was found to be 8.2 percent, by weight, of the paper sample. The residue was then oxidized with dichromate as usual.

⁵ The rosin emulsion was analyzed as follows: 5.00 ml of emulsion was pipetted into a separatory funnel containing ether and dilute hydrochloric acid, and shaken. It was washed once more with very dilute hydrochloric acid, the aqueous portions being extracted with fresh portions of ether. Duplicate determinations gave 0.175 and 0.174 g; average 0.1745 g of resin per 5 ml of emulsion. This analysis was carried out 10 weeks prior to the one described in the preceding section.

⁶ The new method was used for the determination of this small quantity. An error of 100 percent in this value would result in an error of only 0.05 percent in the resin content of the cake. However, errors inherent in the determination of this quantity would cancel, provided that the same method of analysis is used both for the sized and unsized cakes.

(b) COMPARISON WITH THE RESULTS OF OTHER METHODS ON VARIOUS PULPS AND PAPERS

The results of the tests are recorded in table 3. The percentage was calculated on the basis of the oven-dry weight of each material. The materials used were no. 1018, a soda pulp; no. 1017, a sulfite pulp; no. 1014, a paper made from old white rags; and no. 879, a paper made from sulfite pulp. The numbers refer to papers used for other experiments.⁷ The concentration of acids used is expressed in volume-percent.

TABLE 3.—Analytical results on pulps and uncoated and unsurface-sized papers
NO. 1018. SODA PULP

	New method (0.4% hydrochloric acid)		TAPPI method (0.5% acetic acid)		Absolute alcohol (unacidified)		Sutermeister and Torrey (2.5% sulphuric acid)	
	Resin	Equivalent weight	Resin	Equivalent weight	Resin	Equivalent weight	Resin	Equivalent weight
	<i>Percent</i>	<i>g</i>	<i>Percent</i>	<i>g</i>	<i>Percent</i>	<i>g</i>	<i>Percent</i>	<i>g</i>
	0.18	3.49	0.50	6.38	0.34	4.88	-----	-----
	.19	3.87	.51	7.09	.32	4.55	-----	-----
	-----	-----	.49	6.60	-----	-----	-----	-----
Average.....	.18	3.68	.50	6.71	.33	4.71	-----	-----

NO. 1017. SULFITE PULP

	0.72	3.54	1.06	4.96	0.86	3.65	0.73	3.65
	.73	3.70	1.01	4.96	.82	3.93	.75	3.60
	-----	-----	1.00	4.80	.80	3.55	.72	3.60
Average.....	.72	3.62	1.02	4.91	.83	3.71	.73	3.62

NO. 879. SULFITE PAPER

	2.46	3.57	2.40	3.71	1.76	3.65	2.56	3.73
	2.56	3.73	2.43	3.76	1.77	3.49	2.56	3.64
	2.49	3.62	2.57	4.04	1.80	3.44	-----	-----
Average.....	2.50	3.64	2.47	3.82	1.78	3.55	2.56	3.68

NO. 1014. RAG PAPER

	1.92	3.67	1.71	3.65	-----	-----	1.92	3.64
	1.89	3.57	1.88	3.71	-----	-----	1.90	3.52
	1.90	3.62	1.83	3.65	-----	-----	-----	-----
Average.....	1.90	3.62	1.82	3.67	-----	-----	1.91	3.58

The percentages of resin in the pulps determined by the TAPPI method, column 4, are much higher than those found by the other methods, columns 2, 6, and 8. This is due to the fact that the TAPPI extract contains impurities which are carried down by the rather large amount of water present (14 percent), and also by the alcohol. These impurities are not only visible and impart an inhomogeneous and "dirty" appearance to the residues, but also reveal themselves in the high equivalent weights reported in column 5. That a large part of the impurity is due to water is shown by the lower results with a nonaqueous solvent, column 6.

⁷ R. H. Rasch, M. B. Shaw, and G. W. Bicking, *BS J. Research* **11**, (1933) RP574.

M. B. Shaw, G. W. Bicking, and M. J. O'Leary, *J. Research NBS* **14**, 649 (1935) RP794.

The failure of the TAPPI method arises from the fact that all alcoholic solvents also extract materials that are nonresinous, as shown by their insolubility in ether. This is further shown in a consideration of the results with the sulfite paper.

The percentages of resin in the papers, columns 2, 4, 8, using the three acidified solvents are in good agreement. The reason for this apparent contradiction of the findings of Sutermeister and Torrey⁸ that the TAPPI extraction is incomplete, is immediately indicated by the appearance of the TAPPI residues and by their somewhat high equivalent weights, column 5, showing that impurities are present. This is definitely shown by the following experiments: The extractions by the new method and the TAPPI method were carried out on the sulfite paper. The weighed residues were dissolved in ether, which was then washed with water in separatory funnels, evaporated, dried, and weighed. The paper from which the resin had supposedly been extracted by each method was then subjected to a second extraction, but this time by the new method. The results are listed in table 4 and show clearly that the TAPPI solvent fails to extract all of the resin in papers, and that water-soluble impurities are extracted. The results also show that the extracts by the new method contain negligible amounts of water-soluble materials, and that the extraction is practically complete.

TABLE 4.—*Effect of washing the residues obtained by the new and TAPPI methods*

[The results of second extraction on the sulfite paper]

Method	Resin percentage		
	Resin not washed with water	Resin washed with water	Second extraction on paper by the new method
New.....	{ 2.47 2.55 2.46	{ 2.44 2.53 2.44	0.02 .00 .02
Average.....	2.49	2.47	.01
TAPPI.....	{ 2.42 2.46 2.59	{ 2.17 2.20 2.25	0.20 .17 .25
Average.....	2.49	2.21	.21

Extraction by the method of Sutermeister and Torrey⁹ gave the results listed in column 8 of table 3, which were obtained by using an Underwriter siphon cup, a period of steeping overnight, and a 5-hour period of extraction. The results are in good agreement with those of the new method, which has the advantage of being far shorter and simpler, without sacrifice of accuracy.

3. COATED AND SURFACE-SIZED PAPERS

Further test of the new method showed that the results were not affected by the presence of surface-sizing or coating materials. Ordinarily, the presence of such materials necessitates laborious and time-consuming washing of the ether extracts with water.

⁸ E. Sutermeister and W. V. Torrey, Paper Trade J. 94, 33 (January 21, 1932).

⁹ See footnote 8.

All of the results listed in table 5 were obtained by the new method. The materials used were the same two papers described in section IV-2-b, p. 232, but surface-sized or coated, either in the Bureau of Standards paper mill as in the case of no. 1014—glue, or by hand in the laboratory, employing procedures¹⁰ in use at this Bureau.

TABLE 5.—*Analytical results with surface-sized and coated papers, using alcoholic hydrochloric acid (4:1,000)*

Kind of coating or surface sizing	No. 879 sulfite paper			No. 1014 rag paper		
	Amount of coating	Resin	Equivalent weight	Amount of coating	Resin	Equivalent weight
	Percent	Percent		Percent	Percent	
None ^a -----		2.50	3.64		1.90	3.62
Glue-----	{ 4.1	2.38		{ 1.6	1.87	
	{ 4.0	2.43		{ 1.6	1.90	
	{ 4.0	2.49		{ 1.6	1.83	
Average-----		2.43	3.58		1.87	3.56
Starch-----	{ 4.0	2.45		{ 3.5	1.91	
	{ 4.0	2.38		{ 4.0	1.84	
	{ 4.0	2.37		{ 4.0	1.86	
Average-----		2.40	3.60		1.87	3.62
Casein ^b -----	{ 1.5	2.48		{ 1.6	1.94	
	{ 1.6	2.57		{ 1.7	1.98	
	{ 1.5	2.51		{ 1.8	1.92	
Average-----		2.52	3.56		1.95	3.62

^a Results for the untreated papers were taken from table 3.

^b The amounts of casein do not include the clay, which was approximately 10 percent.

If fillers, such as ZnS, CaSO₃, and CaCO₃ are present in paper, the acidity of the extracting solvent is changed unless the filler is first removed by dipping in normal hydrochloric acid, washing and drying. Such treatment was found not to affect the resin content of the paper.

WASHINGTON, December 18, 1936.

¹⁰ For casein see Ind. Eng. Chem. 25, 904 (1933). For glue and starch see footnote 7.